

Porous carbon fibers from copper – substituted plant biomass materials

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Introduction

Novel porous materials based on carbon fibers can find a wide application as an effective sorbents and catalysts. Two different approaches are applied for the preparation of metal-containing porous carbons from cellulosic materials. Some methods are based on introducing of metal compound into cellulosic material with following pyrolysis at elevated temperature [1]. In the this case the simultaneous carbonization of cellulosic material and chemical transformations of introduced metal take place.

The aims of present work include:

- the selection of proper conditions for cellulose and aspen wood oxidative pretreatment with H_2O_2 promoting the formation of surface reactive groups,
- the study of copper influence on the process of Cu-modified cellulosic material carbonization and on the textural characteristics of produced active carbons.

Experimental

Two types of initial cellulosic materials were chosen for investigation: sulfite cellulose with chemical composition (% wt.): cellulose - 90, lignin - 9, ash - 0.9:(including: Ca – 0.3, Mg - 0.3, S - 0.3) and aspen sawdust with composition (% wt.): cellulose 46, hemicellulose – 24, lignin – 22, extractive – 7.5, ash – 0.3 (including Ca –0.2, Mg, Si, S, P, Cu, Fe – 0.1). Before modification and thermal treatment the cellulose was crushed and sieved to particle size 2 x 5 mm, the thickness was varied from 1 to 2 mm. Aspen sawdust fraction ≤ 2 mm was used. The samples were impregnated with aqueous solutions of $Cu(NO_3)_2$, $Cu(CH_3COO)_2$, $Cu(NH_3)_n(OH)_2$ ($n=2,4$) with different concentration. Copper content in solution was varied from 0.1 wt.% to 13.0 wt.%.

Initial and Cu-modified samples were carbonized in quartz reactor with the length 30 mm and diameter 16 mm in a flow of inert gas (N_2 or Ar) using programmed heating with the rate $5^\circ/\text{min}$ and gas flow rate 2.5 l/h. Sample (~ 0.5 g) was located in the hot zone of reactor. The time of treatment at demanded temperature was 2 hours in all cases.

Specific surface area of carbonaceous products was measured by BET method with Ar adsorption at 77 K and following desorption at a room temperature. IR spectra of initial and carbonaceous products were registrated with FTIR- spectrometer Vector 22 Bruker. The samples were pressed into KBr matrix. The thermal decomposition data were obtained by thermogravimetric analysis in the temperature range 20-700 $^\circ\text{C}$ with heating rate $10^\circ/\text{min}$ at air. SEM data were obtained with electronic microscope Jeol-JSM 820. EPR-spectroscopy study was carried out on the spectrometer ER-1307

Results and discussion

In order to select an optimal parameters of pyrolysis process resulting in the formation of porous carbons with high yield and high surface area the influence of carbonisation temperature, rate and time of heating, type of pretreatment and methods of copper introducing into celulosic material was investigated.

It has been found that elevated temperatures ($\sim 700^\circ\text{C}$) promote the formation of porous chars with high surface area (up to 600 $^\circ\text{C}$ m 2 /g from Cu-modified cellulose. Char yield was varied between 16.8 - 23.1 %wt depending on the used method of copper supporting on cellulose. The features of carbonization of copper-modified cellulose were studied by DTA techniques. Some differences between thermal transformation of initial and modified cellulose were observed. For non-modified cellulose the intensive loss of a sample weight connected with the removing of volatile products begins at 280 $^\circ\text{C}$ while the intensive loss of weight for the sample obtained by $Cu(Ac)_2$ supporting on

H₂O₂ treated cellulose starts at 230⁰C. The main weight loss (~88 %) for the modified cellulose samples is accompanied by strong exothermic effect with maximum at 400⁰C. But for initial cellulose sample two exothermic effects accompanying the main weight loss are recorded. The first one (weight loss ~ 52 %) has maximum at 395⁰C, the second one has the maximum at 490⁰C. In this case the loss is ~ 24,6% of total weight of sample. These data indicate on the two-steps thermal destruction of non-modified cellulose.

The obtained results confirm the conclusion made previously [1,2] that the introducing of metal compounds into cellulose results in the shift of the start of thermal decomposition process in the lower temperature region. In the case of studied Cu-substituted cellulose this shift is about 50⁰C. The increased yield of char from Cu-modified samples is connected with catalytic action of copper on the process of cellulose transformation. It seems, the copper promotes predominantly the reaction of condensed compounds formation. FTIR data also indicate that the carbonization of cellulosic matter takes place during thermal treatment, which results in C-O-C bonds destruction and in formation of polyaromatic systems [3]. The growth by 3-5 times of C/H ratio in carbonized Cu-modified products as compared to initial cellulose confirms the high degree of modified samples carbonisation after pyrolysis at 600⁰C.

EPR spectra indicated the presence of individual Cu²⁺ ions with $g_z = 2.37$ and $A_z = 0.0152 \text{ cm}^{-1}$ for all initial Cu-modified samples. But there were no signals indicating the presence of Cu⁺² ions in carbonized samples. It makes possible to suppose that copper is present in these samples both in metallic state and as Cu⁺¹ ions. The performed SEM studies have shown that the carbonaceous products keep morphology structure of the cellulose fibers origin. The values of specific surface areas of chars from the initial and modified cellulose samples were calculated from BET data. Obtained experimental results confirm that copper promotes the formation of extended porosity in carbonized samples.

The influence of nature of Cu-modified cellulosic material on the char yield and its surface area has been studied. The significant differences were observed at pyrolysis temperature 500-600⁰C for modified cellulose and aspen wood. Both the yield of char product and its surface area were higher for aspen-wood sample. The possible reasons at these differences are discussed. Obtained porous carbon fibers have perspectives of the use as sorbents in different technological processes and as novel catalysts or catalyst supports.

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References

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